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ExxonMobil Chemical Europe inc.

P.O. Box 105 1830 Machelen Belgium Ann M. Mareschal

European Patent Attorney Intellectual Property Law Shared Services

+32 2 722 21 04 Telephone +32 2 722 22 99 Facsimile ann.mareschal@exxonmobil.com

European Patent Office Erhardstrasse 27 D-80469 MÜNCHEN GERMANY

ExonMobil 10/582756 AP3 Rec'd PCT/PTO 13 JUN 2006

18 October 2005

International Patent Application No PCT/EP 2004/014477
ExxonMobil Chemical Patents Inc.
Our Ref: 2003B137/WO
RESPONSE TO WRITTEN OPINION OF THE ISA AND FILING OF DEMAND

Dear Sirs,

This communication responds to the Written Opinion of the International Searching Authority that accompanied the International Search Report dated 06 May 2005. In addition we are herewith filing the Demand, together with a Fee Sheet authorising payment of the Demand fee.

The applicants hereby request that a further Written Opinion be issued following substantive examination of the application, bearing in mind the following observations concerning Section V of the Written Opinion.

Where the application is referred to in this communication, reference is made to the text of the application as filed. The application was published on 30 June 2005 with International Publication Number WO 2005/058787 A1.

Amendments

We are filing new pages 33-37 which should replace pages 33-38 currently on file. The new pages constitute a new claim set.

<u>Claim 1</u> now contains the further specification that the hydroformylation is with carbon monoxide and hydrogen, and also the requirements that the hydroformylation product is fed to a high pressure separator, and wherein the carbon monoxide content of the offgas from the high pressure separator is such that the partial pressure of carbon monoxide is above 75 barg.

<u>Claim 18</u> remains dependent on any of the preceding claims, and now contains the requirement that the partial pressure of carbon monoxide is above 77 barg.

<u>Claims 31 and 32</u> represent original claims 32 and 33 respectively. Original claim 31 was removed, and the numbering and dependency of new claims 31 and 32 were adjusted to reflect this removal.

Visiting address:
PC MASTER UPDATERermeslaan 2, 1831 Machelen, Belgium
BTW/TVA: BE 407.625.474
1 9 0 C T 2005 HRB/RCB: 361.301

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There have been no amendments made to any of the claims not specifically mentioned above.

Basis for the amendments in the application as filed

The first feature added to the amended claim 1, specifying that the hydroformylation reaction is with carbon monoxide and hydrogen, finds support in the application on page 1, lines 5-6.

The second feature added to the amended claim 1, requiring that the hydroformylation product is fed to a high pressure separator, finds support on page 20, lines 8-9.

The third feature added to the amended claim 1, requiring that the carbon monoxide content of the offgas from the high pressure separator is such that the partial pressure of carbon monoxide is above 75 barg, finds support on page 24, lines 7-9.

The feature introduced by amended claim 18, requiring that the partial pressure of carbon monoxide is above 77 barg, finds support on page 24, lines 7-10.

Amended claims 31 and 32 find support respectively in claims 32 and 33 as originally filed.

Novelty (Art 33(2) PCT)

<u>Claim 1 as amended is novel over D1 and D2</u> because neither D1 nor D2 specify a partial pressure of carbon monoxide in the processes they disclose.

<u>Claim 1 as amended is novel over D3</u> because D3 discloses partial pressures of carbon monoxide of 8.3 bar abs, or below, i.e. 7.3 bar g or below, which is outside the range specified in claim 1.

<u>Claim 1 is novel over D4, D5 and D6</u> taken individually because the hydroformylation processes disclosed in each of those documents do not involve the recycle of unreacted gases from hydroformylation or a subsequent process stage to at least the hydroformylation reactor in the second position.

The subject matter of claim 1 is therefore novel over the prior art according to Art 33(2) PCT. Claims 2-29 are dependent on claim 1, and are therefore also novel over the prior art.

<u>Claim 30 is novel over D1</u> because the apparatus disclosed in D1 does not comprise means for the removal of catalyst residues from the hydroformylation product and a reactor for hydrogenating the hydroformylation product from which catalyst residues have been removed.

<u>Claim 30 is novel over D2, D3, D4, D5 and D6</u> taken individually because the apparatuses disclosed in each of these documents do not comprise means whereby unreacted hydrogen from

a reactor hydrogenating the hydroformylation product is recycled to the second hydroformylation reactor, if present.

The subject matter of claim 30 is therefore novel over the prior art according to Art 33(2) PCT. Claims 31 and 32 are dependent on claim 30, and are therefore also novel over the prior art.

Inventive Step

Claim 1

D1 may be considered as closest prior art to claim 1, because it is of the same technical field and discloses many features in common with the subject matter of claim 1. When starting from D1, the difference with the subject matter of claim 1 is the requirement that the partial pressure of carbon monoxide is above 75 barg.

D2 may also be considered as closest prior art to claim 1, as it is of the same technical field and again discloses many features in common with the subject matter of claim 1. Also when starting from D2, the difference with the subject matter of claim 1 is again the requirement that the partial pressure of carbon monoxide is above 75 barg.

The effect of this difference is that, if the partial pressure drops below this level, cobalt plating can occur in the hydroformylation reactors (present application, page 24, lines 10-11).

The problem to be solved may therefore be stated as one of how, in the process of D1 or D2, to avoid cobalt plating to occur in the hydroformylation reactors.

This problem is not addressed in any of the cited prior art, nor is the solution to maintain the partial pressure of carbon monoxide above 75 barg. There is therefore nothing in the cited prior art that would allow the skilled reader to arrive at the subject matter of claim 1.

The applicants therefore submit that the subject matter of claim 1 is inventive over the prior art according to Art 33(3) PCT. Claims 2-29 are dependent on claim 1, and derive their inventiveness at least from this dependency.

Claim 30

D1 is considered the closest prior art to claim 30, because it is of the same technical field and discloses many features in common with the subject matter of claim 30. The difference with claim 30 is the means for removal of catalyst residues from the hydroformylation product.

The effect of this difference is that the process of the invention offers a free choice of catalyst for the hydrogenation reaction, as opposed to D1 where the catalyst is necessarily a slurry of

supported cobalt metal. More suitable catalysts may be selected, such as those catalysts that may be provided in a fixed bed and are also capable of converting formate esters made in hydroformylation to alcohols (see present application, page 6, lines 4-5).

The problem to be solved may therefore be stated as one of how, in the apparatus of D1, other catalysts may be allowed in the hydrogenation reactor, including fixed bed catalysts.

This problem is not addressed in any of the cited prior art. There is therefore nothing in the cited prior art that would allow the skilled reader to arrive at the subject matter of claim 30.

The applicants therefore submit that the subject matter of claim 30 is inventive over the prior art according to Art 33(3) PCT. Claims 31 and 32 are dependent on claim 30, and derive their inventiveness at least from this dependency.

Summary

The applicants submit that, for the reasons given above, the claimed invention is clearly defined, novel and inventive.

The applicants hereby request that any further Written Opinion to be issued by the IPEA takes account of the above arguments.

Please return Form 1037 to acknowledge receipt.

Yours faithfully,

Mareschal, Ann

Doverdal

General Authorisation Number 41236

Encl.: Demand

New pages 33-37

Fee Sheet Form 1037

CLAIMS

- 1. A process comprising the hydroformylation of one or more olefins with carbon monoxide and hydrogen to form a hydroformylation product, wherein the hydroformylation takes place in a series of at least two hydroformylation reactors, wherein unreacted gases from hydroformylation or a subsequent process stage are recycled to at least the hydroformylation reactor in the second position, whereby the hydroformylation product is fed to a high pressure separator, and wherein the carbon monoxide content of the offgas from the high pressure separator is such that the partial pressure of carbon monoxide is above 75 barg.
- 2. The process according to claim 1 comprising a stage for hydrogenating the hydroformylation product to form alcohols, which process comprises catalytically hydroformylating the olefin(s), removing catalyst residues from the hydroformylation product to form a substantially catalyst-free hydroformylation product, and subsequently hydrogenating the substantially catalyst-free hydroformylation product, wherein the unreacted gases that are recycled comprise unreacted hydrogen from the hydrogenation stage.
- 3. The process according to claim 2 wherein the unreacted gases that are recycled comprise unreacted gases from the hydroformylation reaction and unreacted hydrogen from the hydrogenation stage.
- 4. The process according to any of the preceding claims wherein the hydroformylation is a high or medium pressure hydroformylation process in which the olefin(s) are reacted with carbon monoxide and hydrogen in the presence of a hydroformylation catalyst, wherein feed to the first reactor comprises a mixture of:
 - i. olefin(s)
 - ii. carbon monoxide
 - iii. hydrogen
 - iv. recycle gases comprising unreacted gaseous materials from the hydroformylation reaction;

and the feed to the reactor in the second position comprises a mixture of:

i.the reaction product from the first reactorii.recycle gases comprising unreacted gaseous materials from the hydroformylation reaction.

5. The process according to claim 4 in which the hydroformylation is performed in a series of at least three reactors and the feed to the reactor in the third position comprises:

i.the reaction product from the reactor in the second position ii.recycle gases comprising gaseous materials from the hydroformylation reaction.

- 6. The process according to claim 4 or 5 in which the hydroformylation is performed in a series of four reactors and the feed to the reactor in the fourth position consists of the reaction product from the reactor in the third position.
- 7. The process according to any of the preceding claims in which the hydroformylation is performed at a pressure of from 50 to 350 barg, preferably 250 to 350 barg, most preferably from 275 to 325 barg.
- 8. The process according to any of the preceding claims in which the hydroformylation is performed at a temperature of from 120 to 185°C, preferably from 170 to 180°C.
- 9. The process according to any of the preceding claims employing a hydroformylation catalyst, in which the catalyst supplied is absorbed in the olefin feed.

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- 10. The process according to any of the preceding claims employing a hydroformylation catalyst which comprises a rhodium catalyst or a cobalt catalyst, particularly those selected from hydrocobaltcarbonyl or rhodium carbonyls.
- 11. The process according to claim 10 in which the catalyst is a cobalt catalyst and the molar ratio of hydrogen to carbon monoxide in the syngas used for hydroformylation is about 1.3:1.
- 12. The process according to claim 10 or 11 in which the catalyst is a cobalt catalyst and the hydroformylation product is purified by injection of caustic soda and/or sodium carbonate into the hydroformylation reaction product in a decobalter vessel.
- 13. The process according to claim 12 in which a stoichiometric excess of 100 to 200%, particularly 140 to 180% of sodium hydroxide or carbonate is used.
- 14. The process according to claim 12 or 13 in which the decobalter is operated at a temperature in the range 155-165°C.
- 15. The process according to claim 10 or 11 in which the catalyst is a cobalt catalyst, and the cobalt is removed by an acidic and/or oxidative method.
- 16. The process according to claim 15 wherein the acidic method uses formic and/or acetic acid.
- 17. The process according to claim 15 or 16 wherein the oxidative method uses oxygen, an oxygen containing gas, or air.
- 18. The process according to any of the preceding claims wherein the partial pressure of carbon monoxide is above 77 barg.

- 19. The process according to claim 18 in which the high pressure separator operates at a pressure of 250 barg or higher, preferably a pressure in the range 250 to 300 barg, more preferably 260 to 270 barg.
- 20. The process according to claim 18 or 19 in which the quantity of high pressure gas required for recycle is sent to an offgas recycle compressor system.
- 21. The process according to any of claims 18 to 20 in which the liquid left in the high pressure separator is fed to an intermediate pressure separator where the pressure is reduced to a level at which gases dissolved or entrained in the liquid from the high pressure separator are released as an intermediate pressure offgas.
- 22. The process according to claim 21 in which the pressure in the intermediate pressure separator is between 80 and 120 barg, preferably between 90 and 110 barg.
- 23. The process according to claim 21 or 22 in which at least a portion of the intermediate pressure offgas is sent to an offgas recycle compressor system for subsequent recycle.
- 24. The process according to any of the preceding claims in which the recycle employs a compressor system comprising a series of gas compressor stages in which the pressure is gradually increased to the pressure required in the hydroformylation reaction.
- 25. The process according to claim 24 in which the recycle compressor system comprises three gas compressor stages in series.
- 26. The process according to claim 25 in which high pressure offgas and intermediate pressure offgas from the hydroformylation step are fed (together with unreacted gas from the hydrogenation stage, when present) to the first compressor stage which preferably operates at a suction pressure between 50 and 60 barg.

- 27. The process according to claim 26 in which the gas mixture discharged from the first compressor stage is fed, optionally with intermediate pressure offgas, to the second compressor stage where the pressure is increased to within the range 140 to 180 barg, preferably 150 to 170 barg.
- 28. The process according to claim 27 in which the gas mixture discharged from the second compressor stage is fed, optionally with high pressure offgas, to the third compressor stage.
- 29. The process according to any of the preceding claims wherein duplex stainless steel is used as material of construction for at least one piece of the hydroformylation reactors or any of their associated equipment.
- 30. An apparatus for the production of alcohols from an olefin, comprising a series of at least two reactors for catalytic hydroformylation of olefin, means for the removal of catalyst residues from the hydroformylation product, a reactor for hydrogenating the hydroformylation product from which catalyst residues have been removed, and means whereby unreacted hydrogen from the hydrogenation reactor is recycled to at least the second hydroformylation reactor.
- 31. The apparatus according to claim 30 which comprises both means for recycling unreacted hydrogen from the hydrogenation reactor, and means for recycling unreacted gases from the hydroformylation reaction.
- 32. The apparatus according to claim 30 or 31 wherein duplex stainless steel is used as material of construction for at least one piece of the hydroformylation reactors or any of their associated equipment.

The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/EP

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:

The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty.

Fo	r International Preliminar	y Examining Authorit	y use only			
			•			
Identification of IPEA		Date of receipt of D	EMAND			
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPL		APPLICATION	Applicant's or agent's file reference 2003B137			
International application No.	International filing date		(Earliest) Priority date (day/month/year)			
PCT/EP2004/014477	16 December 200	04 (16/12/2004)	18 December 2003 (18/12/2003)			
Title of invention IMPROVEMENTS IN OR RELATING TO HYDROFORMYLATION						
Box No. II APPLICANT(S)						
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)			Telephone No.			
ExxonMobil Chemical Paten			Facsimile No.			
5200 Bayway Drive			·			
Baytown, TX 77520-5200			Teleprinter No.			
United States of America			Applicant's registration No. with the Office			
		T				
State (that is, country) of nationality: US		State (that is, count.	ry) of residence:			
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) BEADLE, Stephen W. 36173 Bluff Oaks Avenue Prairieville 70769 Louisiana USA						
State (that is, country) of nationality:		State (that is, count	ry) of residence:			
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)						
GARTON, Ronald D. 8350 Myrtelake Drive Baton Rouge 70810 Louisiana USA						
State (that is, country) of nationality: US		State (that is, country	v) of residence:			
Further applicants are indicated or	a continuation sheet.					

Sheet No. ..2

International application No. PCT/EP2004/014477

Continuation of Box No. II APPLICANT(S)				
If none of the following sub-boxes is used, this sheet should not be included in the demand.				
Name and address: (Family name followed by given name: for a legal entity, for BECKERS, Hubertus J. Bollostraat 6 3140 Keerbergen Belgium	ull official designation. The address must include postal code and name of country.)			
State (that is, country) of nationality: NL	State (that is, country) of residence: BE			
Name and address: (Family name followed by given name; for a legal entity,) CAERS, Raphael Frans Prins Boudewijnlaan 189 2650 Edegem Belgium	full official designation. The address must include postal code and name of			
State (that is, country) of nationality: BE	State (that is, country) of residence: BE			
Name and address: (Family name followed by given name; for a legal entity, for country.) VAN VLIET, Arie Parklaan 51 3080 Tervuren Belgium	idl official designation. The address must include postal code and name of			
State (that is, country) of nationality: NL	State (that is, country) of residence: BE			
Name and address: (Family name followed by given name; for a legal entity, for HOUBEN, John J. Heer Bokelweg 196 3032 AD Rotterdam Netherlands	ull official designation. The address must include postal code and name of country.) .			
State (that is, country) of nationality: NL	State (that is, country) of residence: NL			
Further applicants are indicated on another continuation sheet.				

Sheet No. ..3

International application No. PCT/EP2004/014477

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE					
The following person is agent common representative					
and has been appointed earlier and represents the applicant(s) also for international preliminary examination.					
is hereby appointed and any earlier appointment of (an) agent(s)/common repres	entative is hereby revoked.				
is hereby appointed, specifically for the procedure before the International Prelimination and the agent(s)/common representative appointed earlier.	ninary Examining Authority, in addition to				
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)	Telephone No. +32 2 722 22 24				
DEW, Melvyn John	Facsimile No.				
ExxonMobil Chemical Europe Inc.	+32 2 722 22 99				
PO Box 105	Teleprinter No.				
B-1830 Machelen					
Belgium	Agent's registration No. with the Office				
Address for correspondence: Mark this check-box where no agent or common space above is used instead to indicate a special address to which correspondence					
Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION					
Statement concerning amendments:*					
The applicant wishes the international preliminary examination to start on the basis of	f:				
the international application as originally filed					
the description as originally filed					
as amended under Article 34	• •				
the claims as originally filed					
as amended under Article 19 (together with any accompany)	ng statement)				
as amended under Article 34					
the drawings					
as originally fried as amended under Article 34					
 The applicant wishes any amendment to the claims under Article 19 to be considered as reversed. Where the IPEA wishes to start the international preliminary examination at the same time as the international search in 					
accordance with Rule 69.1(b), the applicant requests the IPEA to postpone the start of the international preliminary examination until the expiration of the applicable time limit under Rule 69.1(d).					
4. The applicant expressly wishes the international preliminary examination to start earlier than at the expiration of the applicable time limit under Rule 54bis.1(a).					
* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.					
Language for the purposes of international preliminary examination: .English					
which is the language in which the international application was filed.					
which is the language of a translation furnished for the purposes of international search.					
which is the language of publication of the international application.					
which is the language of the translation (to be) furnished for the purposes of international preliminary examination.					
Box No. V ELECTION OF STATES					
The filing of this demand constitutes the election of all Contracting States which are designated and are bound by Chapter II of the					
PCT.					

Sheet No 4			PCT/EP2004/014477		
Box No. VI CHECK LIST	-				
The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:				For International Preliminary Examining Authority use only received not received	
1. translation of international application	:	sheets			
2. amendments under Article 34	:	sheets			
copy (or, where required, translation) of amendments under Article 19	:	sheets			
 copy (or, where required, translation) of statement under Article 19 	:	sheets			
5. letter	:	sheets			
6. other (specify) Form 1037	:	2 sheets			
The demand is also accompanied by the item(s) ma	arked below:				
1. fee calculation sheet	1. x fee calculation sheet 5. statement explaining lack of signature				
2. original separate power of attorney	6 sequence listing in electronic form				
3. original general power of attorney	7. tables in electronic form related to a sequence listing				
4. copy of general power of attorney; reference number, if any:		8. x other (specify,): Response to IS	SA Written Opinion	
Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).					
Melvyn John GA No 11495					
For Internation	nal Preliminar	y Examining Authority u	se only		
Date of actual receipt of DEMAND:					
Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):					
3. The date of receipt of the demand is expiration of 19 months from the priori item 4 or 5, below, does not apply.		expiration	of receipt of the de of the time limit unde 8, below, does not ap	mand is AFTER the or Rule 54 <i>bis</i> .1(a) and oply.	
The applicant has been informed accordingly. The date of receipt of the demand is WITHIN the time			er Rule 54bis.1(a) as	nd is WITHIN the time extended by virtue of	
limit of 19 months from the priority date by virtue of Rule 80.5. Although the date of receipt of the dema expiration of 19 months from the prio delay in arrival is EXCUSED pursuant	nd is after the ity date, the	expiration		the demand is after the er Rule 54 <i>bis</i> .1(a), the pursuant to Rule 82.	
For International Bureau use only					
Demand received from IPEA on:					
Form PCT/IPEA/401 (last sheet) (April 2005)			See i	Notes to the demand form	

C. MACK

CHAPTER II

PCT

FEE CALCULATION SHEET

Annex to the Demand

	For International Preliminary Examining Authority use only		
International application No. PCT/EP2004/014477			
Applicant's or agent's file reference 2003B137	Date stamp of the IPEA		
Applicant			
ExxonMobil Chemical Patents Inc.			
CALCULATION OF PRESCRIBED FEES			
Preliminary examination fee	1530.00 P		
2. Handling fee (Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.)	129.00 H		
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	1659.00 TOTAL		
MODE OF PAYMENT			
authorization to charge deposit account with the IPEA (see below) cheque revenue star postal money order coupons bank draft other (species			
AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT AG (This mode of payment may not be available at all IPEAs)	CCOUNT IPEA/ EP		
Authorization to charge the total fees indicated above.	Deposit Account No.: 28300203		
(This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.	Date: 18 October 2005 Name: DEW, Melvyn John Signature: Melvyn Deux		

Form PCT/IPEA/401 (Annex) (April 2005)

See Notes to the fee calculation sheet